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"Dyeing process using a specific compound containing active methylene and a compound chosen from an aldehyde, a ketone, a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative"

Inventors:

"Dyeing process using a specific compound containing active methylene and a compound chosen from a specific aldehyde, a specific ketone, a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative"

The present invention relates to the use, for dyeing keratin fibres, of at least one specific compound containing active methylene and of at least
5 one compound chosen from an aldehyde, a ketone, a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative, to dye compositions comprising a combination of these compounds, to dyeing processes using the said compounds and to a multi-compartment
10 device containing these compounds.

It is known practice, for the dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, to use direct dyes or coloured substances which give the fibres a temporary or semi-permanent
15 coloration, of low dyeing power, which is generally removed by washing or perspiration. The range of shades obtained by these direct processes are generally limited. It is also known practice to use oxidation dyes (oxidation bases and couplers), which are
20 compounds which are initially colourless or weakly coloured and which, under the action of an oxidizing agent, generate coloured compounds by a process of oxidative condensation. Compared with direct colorations, oxidative colorations are permanent,
25 powerful and withstand external agents (light, bad weather, washing, perspiration and rubbing). Nevertheless, the use of the oxidizing agent can harm the keratin fibres and make the processes for carrying out the oxidative dyeing operations relatively complex.

30 The Applicant has just discovered a novel dyeing process, which does not involve a process of oxidative development of dyes, and which gives a wide range of shades.

The compounds used by the Applicant are small
35 molecules which can penetrate into keratin easily. The

Applicant has found, surprisingly, that these compounds can then condense to form chromophores or dyes, bulkier molecules which remain trapped inside the keratin.

The Applicant has thus found that the dyes
5 obtained withstand shampooing and perspiration and are stable with respect to light, bad weather and chemical agents. The Applicant has, in a way, discovered a novel dyeing process which has the advantages of so-called oxidation dyeing without exhibiting its drawbacks,
10 since no oxidizing agent is used.

One subject of the present invention is thus the use, for dyeing keratin fibres, of a specific compound containing active methylene and of a compound chosen from a specific aldehyde, a specific ketone, a
15 quinone and a diiminoisoindoline or 3-aminoisoindolone derivative.

Another subject of the invention relates to dye compositions comprising these compounds.

A subject of the present invention is also a
20 process for dyeing keratin fibres, which consists in applying a specific compound containing active methylene and a compound chosen from a specific aldehyde, a specific ketone, a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative to
25 the fibres, either simultaneously, in the form of a mixture prepared at the time of use, or successively.

Another subject of the invention also consists of a dyeing agent for carrying out the process of the invention.

30 Other subjects of the invention will become apparent in the light of the description.

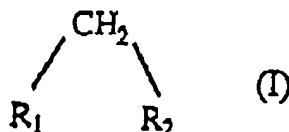
The main subject of the present invention is thus the use, for dyeing keratin fibres, in particular human keratin fibres such as the hair, of at least one
35 specific compound containing active methylene and of at least one compound chosen from an aldehyde, a ketone, a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative, in order to obtain, by reaction without an

oxidizing agent, a coloration of the said keratin fibres.

In the context of the present invention, a compound containing active methylene is defined as a methylene group substituted with two groups with an electron-withdrawing effect or mesomeric effect. Such compounds are described in particular in Advanced Organic Chemistry Jerry March, 4th edition, Wiley Intersciences, pages 279, 741 and 795.

The compounds containing active methylene of the present invention are chosen more particularly from:

1) the compounds of formula (I) below:

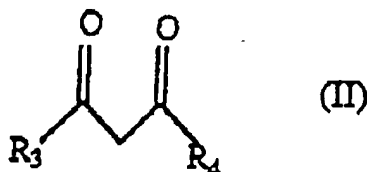


in which:

R_1 denotes a group $-\text{COR}$ or $-\text{COOR}$ with R denoting a hydrogen atom or an alkyl group,

R_2 denotes the groups denoted by R_1 , a nitrile group, a substituted or unsubstituted aryl or alkylaryl group, or a substituted or unsubstituted heterocycle;

2) the compounds of formula (II) below:

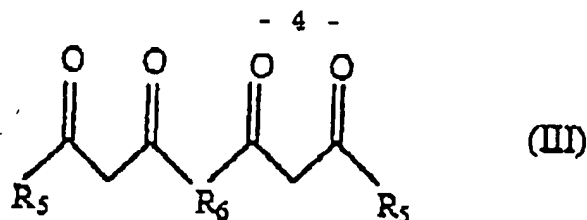


in which:

R_3 denotes the groups denoted by R_2

R_4 denotes a substituted or unsubstituted alkyl group, an acetyloxy group, a cycloalkyl group, a substituted or unsubstituted alkylaryl group, an aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted aminoaryl group or a substituted or unsubstituted heterocycle;

3) the compounds of formula (III) below:

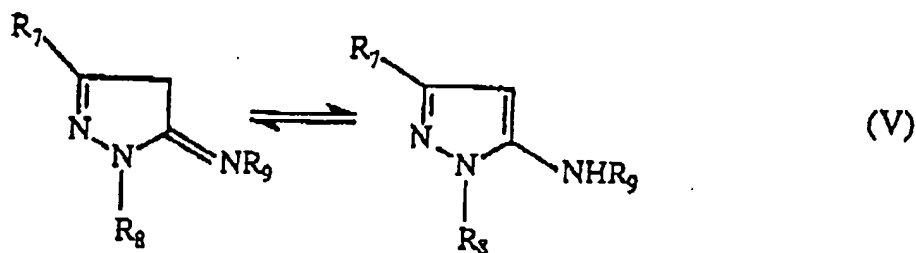
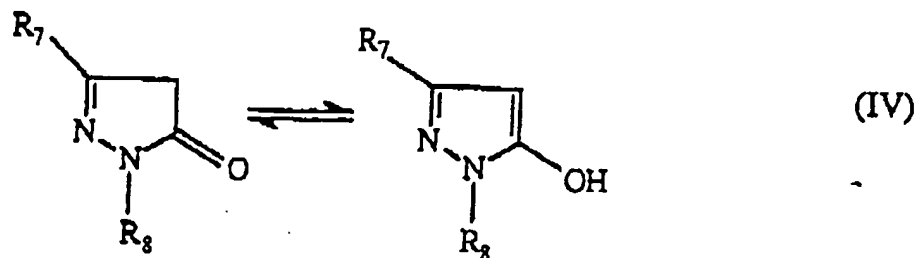


in which:

R_5 denotes the groups denoted by R_2

R_6 denotes a substituted or unsubstituted aryl or aralkyl group, a substituted or unsubstituted aminoaryl group or a substituted or unsubstituted heterocycle;

4) the pyrazole derivatives (i) of formulae (IV) and (V) below:



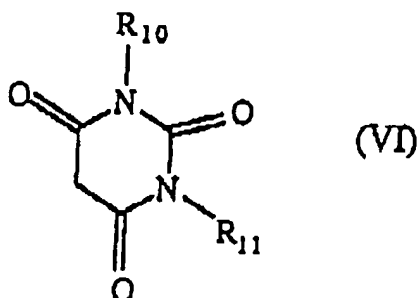
10 in which:

R_7 and R_8 , which may be identical or different, denote the groups denoted by R_4 ,

R_9 denotes a hydrogen atom or a substituted or unsubstituted alkyl group;

15 and (ii) formed by two pyrazole rings of formula (IV) or (V) linked by R_7 or R_8 ;

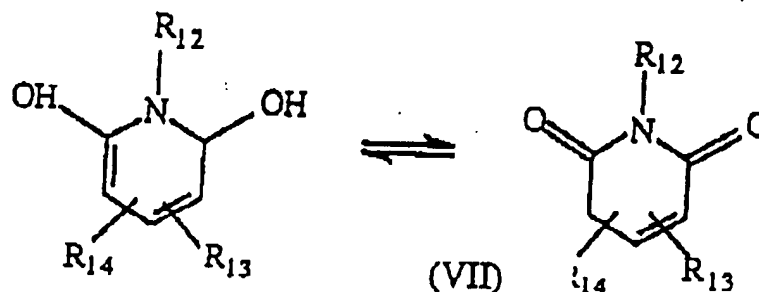
5) the barbituric acid derivatives (i) of formula (VI) below:



in which:

R_{10} and R_{11} , which may be identical or different, denote a substituted or unsubstituted alkyl group, an alkenyl group, a cycloalkyl group, an alkylaryl group or a substituted or unsubstituted aryl group, and (ii) the compounds formed by two rings of formula (VI) linked by R_{10} or R_{11} ;

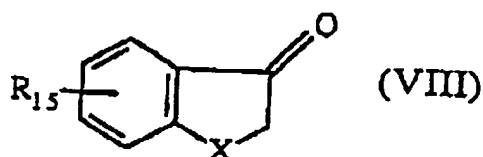
6) the pyridine derivatives of formula (VII):



in which:

R_{12} denotes a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group;
 R_{13} denotes a hydrogen atom, a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group;
 R_{14} denotes a hydrogen atom, a nitrile group, a substituted or unsubstituted alkyl group, or a group COOR, R denoting a hydrogen atom or a substituted or unsubstituted alkyl group;

7) the derivatives of formula (VIII) below:

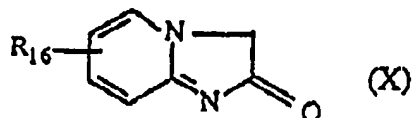
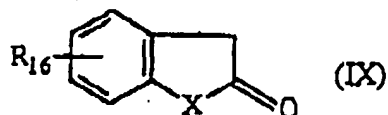


in which:

X denotes an oxygen, sulphur or nitrogen atom or a group NR', R' denoting an alkyl group,

R₁₅ denotes a hydrogen, chlorine or bromine atom or a hydroxyl, nitro, alkyl, alkoxy, carboxamide, sulphonamide or nitrile group;

8) the derivatives of formulae (IX) and (X) below:

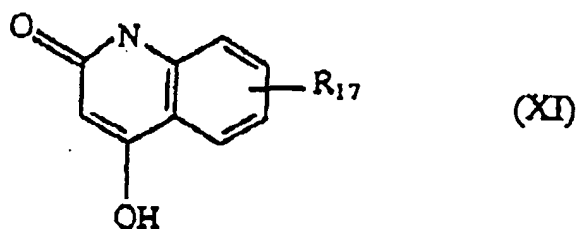


in which:

10 X denotes an oxygen, sulphur or nitrogen atom or a group NR', R' denoting an alkyl group,

R₁₆ denotes the atoms and groups denoted by R₁₅;

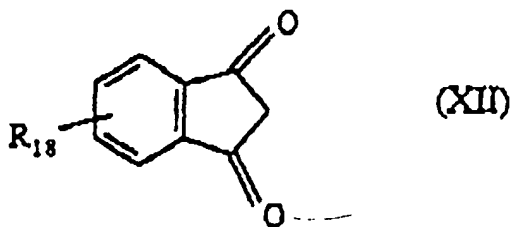
9) the derivatives of formula (XI) below:



15 in which:

R₁₇ denotes a hydrogen atom, a hydroxyl group, a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl or alkylaryl group;

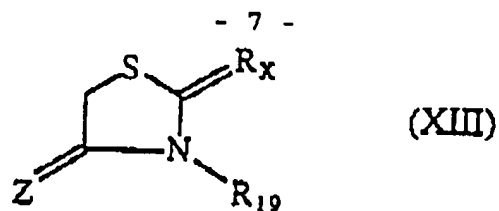
10) the indanedione derivatives of formula (XII) below:



in which:

R₁₈ denotes a hydrogen, chlorine or bromine atom or a nitro, alkyl, alkoxy, carboxamide, sulphonamide or nitrile group;

11) the derivatives of formula (XIII) below:



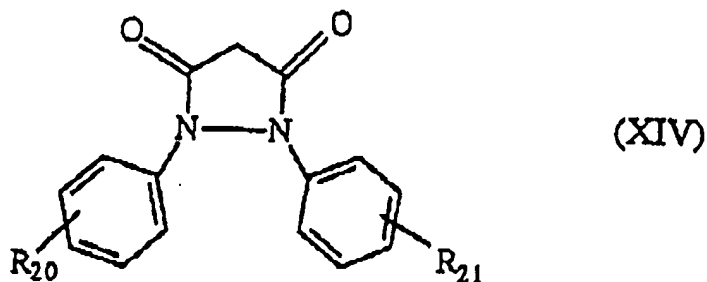
in which:

Z denotes O or NR with R = H or alkyl

R_x denotes a sulphur atom or NR, R denoting a hydrogen atom or an alkyl group;

R_{19} denotes a hydrogen atom or an alkyl, alkoxy, nitro or nitrile group;

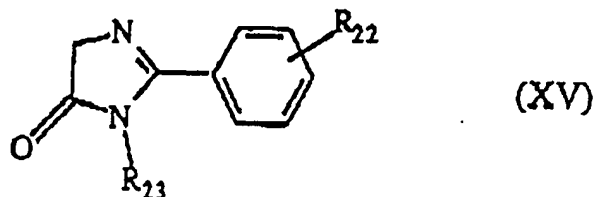
12) the dioxopyrazole derivatives of formula (XIV) below:



in which:

R_{20} and R_{21} , which may be identical or different, denote a hydrogen atom or an alkyl, alkoxy, nitro or nitrile group;

13) the 5-oxoimidazole derivatives of formula (XV) below:

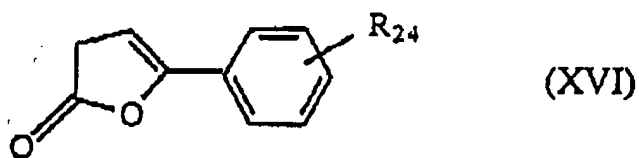


in which:

R_{22} denotes a hydrogen atom or an alkyl group

R_{23} denotes a hydrogen atom or an alkyl, alkoxy, nitro or nitrile group;

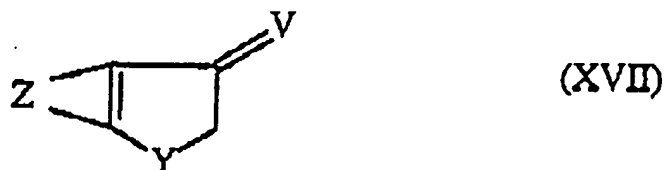
14) the dehydrobutyrolactone derivatives of formula (XVI) below:



in which:

R_{24} denotes a hydrogen atom or an alkyl, alkoxy, nitro or nitrile group;

5 15) the compounds of formula (XVII) below:



in which:

Z forms an aromatic ring

V denotes an oxygen atom or a group $A \text{---} E$

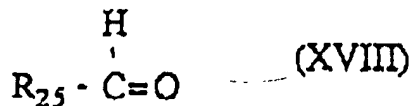
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in which A or E denotes a substituent having a Hammett constant of between 0.4 and 2.0 or substituents for which the sum of the Hammett constants is between 0.4 and 2.0

15 Y denotes Co, O, S or NR_1 , when V is other than an oxygen atom, or denotes CS, $C = NR_2$, SO or SO_2 , with R_1 or R_2 denoting a hydrogen atom or an alkyl radical; and from the cosmetically acceptable salts of the compounds defined above.

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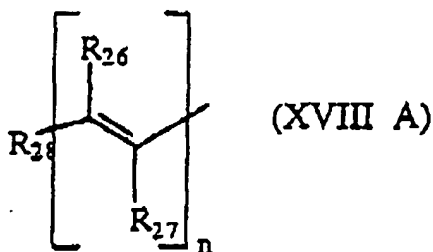
They are used in combination with at least one aldehyde corresponding to formula (XVIII) below:



in which:

25

R_{25} denotes a group of formula (XVIII A) below:



in which

R_{26} and R_{27} , which may be identical or different, denote a hydrogen atom or an alkyl, mono- or polyhydroxyalkyl, alkylhydroxyalkyl, alkoxy, $-\text{CF}_3$ or $-\text{OCF}_3$ group,

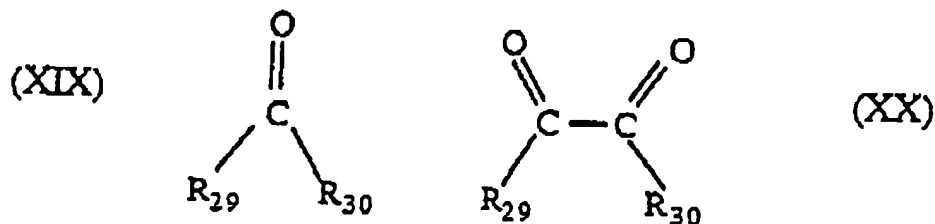
R_{26} and R_{27} can also form, together with the atoms to which they are attached, a 5- or 6-membered heterocyclic or aryl ring, the said rings possibly being substituted or unsubstituted;

n denotes an integer from 0 to 3,

R_{28} denotes the substituents denoted by R_{26} , a substituted or unsubstituted aryl or alkylaryl group or a substituted or unsubstituted 5- or 6-membered heterocyclic group,

or with the cosmetically acceptable salts of these compounds;

a ketone corresponding to formulae (XIX) or (XX) below:



in which:

R_{29} denotes the substituents denoted by R_{26} ,

R_{30} denotes an alkyl, mono- or polyhydroxyalkyl, or hydroxyalkyl group or a substituted or unsubstituted aryl, alkylaryl or 5- or 6-membered heterocyclic group,

R_{29} and R_{30} can also form, together with the atoms to which they are attached, a 5- or 6-membered aryl ring or a heterocyclic ring comprising hetero atoms such as N or S, it being possible for the said ring itself to be attached to a 5- or 6-membered aryl ring or to a

heterocycle comprising hetero atoms such as N or S, the said rings possibly being substituted or unsubstituted, or with the cosmetically acceptable salts of these compounds,

- 5 - a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative, making it possible to obtain, by reaction without an oxidizing agent, a coloration of the said keratin fibres.

- 10 Among the compounds of formulae (I), (II) and (III) which may be mentioned in particular are malonic acid and its esters and acetoacetic acid and its derivatives.

- The compounds of formula (IV) may be, in particular, the following: pyrazolone(5),
15 3-methylpyrazolone(5), 1-phenyl-3-methylpyrazolone(5),
1-(b-cyanethyl)-3-methylpyrazolone(5),
1,3-dimethylpyrazolone(5), 1-(b-acetoxyethyl)-
3-methylpyrazolone(5), 1-(o-chlorophenyl)-
3-methylpyrazolone(5), 1-phenyl-3-carbomethoxy-
20 pyrazolone(5), 1-(3-aminophenylpyrazolone(5),
1-(4-aminophenyl)pyrazolone(5), 3-methylpyrazolone(5)-
1-carboxamide, 1-phenylpyrazolone(5)-3-carboxamide,
aminopyrazole, 1-phenyl-5-aminopyrazole, 1-benzyl-5-
aminopyrazole, 1-cyclohexyl-5-aminopyrazole, 1-ethyl-
25 3-methyl-5-aminopyrazole, 1-benzyl-3-phenyl-
5-aminopyrazole, 1-isopentyl-5-aminopyrazole,
1-furfuryl-5-aminopyrazole, 2-methyl-4H-pyrazolo(5)-
[2,3-a]-benzimidazole, [1-(3-thiacyclopentyl)-
3-methylpyrazolone(5) S-dioxide] and 2-methyl-1H-
30 3,3a,8-triazacyclopenta[a]indene.

- The barbituric acid derivatives of formula (VI) can be chosen from di-n-butyl-, diisobutyl-, di-N-amyl-, diisoamyl-, di-n-hexyl-, dibenzyl-, di-β-phenylethyl-, dicyclohexyl-, diphenyl-,
35 di-p-tolyl- and di-p-methoxybenzyl-barbituric acids; N-methyl-N'-n-butyl-, N-methyl-N'-benzyl-, N-methyl-N'-β-phenylethyl-, N-methyl-N'-γ-phenylpropyl-, N-methyl-N'-γ-phenylbutyl-, N-methyl-N'-α-isobutyl-γ-phenylpropyl-, N-methyl-N'-cyclohexyl-, N-methyl-N'-

phenyl-, N-methyl-N'-p-tolyl- and N-methyl-N'-norbornylmethyl-barbituric acids and the corresponding N-ethyl and N-n-butyl derivatives.

The pyridines and pyridones of formula (VII) may be, for example, 2,6-dihydroxy-3-cyano-4-methylpyridine, those of the cyanopyridone, aminonitropyridone and aminocyanopyridone families and in particular: N-methyl-3-cyano-4-methyl-6-hydroxy-2-pyridone, N-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone, N-b-methoxyethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone, 2,6-dihydroxy-3-cyano-4-methylpyridine, N-b-hydroxyethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone, N-butyl-3-cyano-4-methyl-6-hydroxy-2-pyridone and N-phenyl-3-cyano-4-methyl-6-hydroxy-2-pyridone.

The derivatives of formula (VIII) can be chosen in particular from 6-hydroxybenzofuran-(2H)-one and benzofuran-(2H)-one.

The derivatives of formula (IX) may be, for example:

- 1,3-dihydroindol-2-one
- 3H-benzofuran-2-one
- 1-methyl-1,3-dihydroindol-2-one
- 5-methoxy-3H-benzofuran-2-one
- 5-nitro-1,3-dihydroindol-2-one
- 1-methyl-5-nitro-1,3-dihydroindol-2-one
- 6-methoxy-1,3-dihydroindol-2-one
- 5-chloro-1,3-dihydroindol-2-one
- 5,6-difluoro-1,3-dihydroindol-2-one
- 6-hydroxy-5-methoxy-1,3-dihydroindol-2-one
- 5,6-dimethoxy-1,3-dihydroindol-2-one
- 6-trifluoromethyl-1,3-dihydroindol-2-one.

Derivatives of formula (X) may be, for example:

- imidazo[1,2-a]pyridin-2-one
- 6-bromoimidazo[1,2-a]pyridin-2-one.

The derivatives of formula (XI) are preferably chosen from the derivatives for which R_1 denotes a hydrogen atom, such as, for example, 2,4-dihydroxyquinoline.

The derivatives of formula (XII) correspond in particular to 1',1,3-indanedione.

The derivatives of formula (XIII) are preferably chosen from rhodamine and 4-imino-
5 4,5-dihydrothiazol-2-ylamine.

A derivative of formula (XIV) which may be mentioned is 1,2-diphenyldioxopyrazole.

The derivatives of formula (XV) are chosen in particular from:

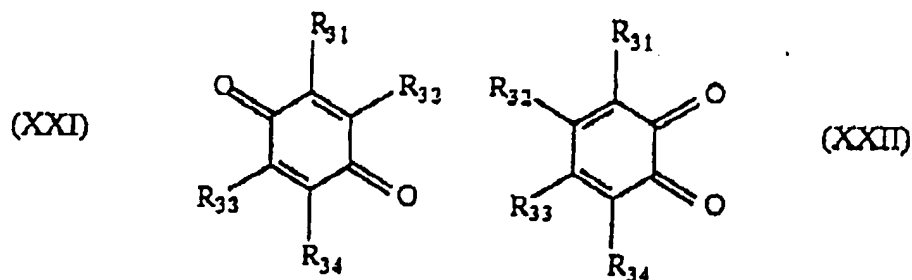
- 10 - 2-phenyl-3,5-dihydroimidazol-4-one
- 3-methyl-2-p-tolyl-3,5-dihydroimidazol-4-one.

A preferred compound of formula (XVI) which may be mentioned is phenyldihydrobutyrolactone.

Preferred compounds of formula (XVII) which may
15 be mentioned are:

1,1-dioxo-1,2-dihydro-11,6-benzo[b]thiophen-3-one and
2-(1,1-dioxo-1,2-dihydro-11,6-benzo[b]thiophen-
3-ylidene)malononitrile.

20 The quinone can correspond to formulae (XXI) and (XXII) below:



in which:

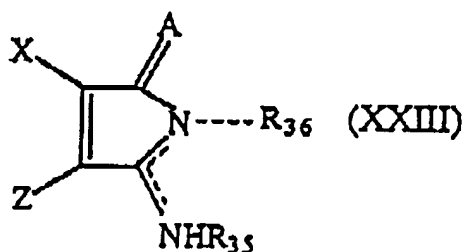
R₃₁ denotes a hydrogen or halogen atom or a sulphonic or
25 alkoxy group,

R₃₂, R₃₃ and R₃₄, which may be identical or different, denote a hydrogen or halogen atom, a hydroxyl, alkyl, mono- or polyhydroxyalkyl, alkylhydroxyalkyl, alkylsulphonyl, carboxyalkyl, aminoalkyl, alkylaminoalkyl,
30 (dihydroxy)alkylaminoalkyl or alkyl-NR'R" group (with R' and R" denoting alkyl or possibly forming, together with the nitrogen atom to which they are attached, an aryl ring or a 5- or 6-membered heterocycle), an aryl

group or an amino group which can be substituted with an alkyl or a hydroxyalkyl,

R_{31} and R_{32} , R_{31} and R_{33} or R_{33} and R_{34} can form, together with the atoms to which they are attached, a substituted or unsubstituted aryl ring or 5- or 6-membered heterocycle;
or to the cosmetically acceptable salts of these compounds.

The diiminoisoindoline or 3-aminoisoindolone derivatives can be those corresponding to formula (XXIII) below:



in which:

R_{35} and R_{36} , which may be identical or different, denote a hydrogen atom, an alkyl, mono- or polyhydroxyalkyl, alkylhydroxyalkyl, aminoalkyl, alkylaminoalkyl or (dihydroxy)alkylaminoalkyl group or an alkyl-NR'R" group, with R' and R" denoting alkyl or possibly forming, together with the nitrogen atom to which they are attached, an aryl ring or a 5- or 6-membered heterocycle,

A denotes an oxygen atom or NH,

X and Z together form a substituted or unsubstituted aryl ring or a 5- or 6-membered heterocycle;

or to the cosmetically acceptable salts of these compounds.

Among the preferred compounds of formula (XVIII) which may be mentioned in particular are benzaldehyde, 2,3,4-monohydroxybenzaldehydes, 2,3,4-monomethoxybenzaldehydes, 2,3,4-monomethylbenzaldehydes, (2,3)-, (2,4)-, (2,5)-, (2,6)- and (3,5)-dihydroxybenzaldehydes, (2,3)-, (2,4)-, (2,5)-, (2,6)- and (3,5)-dimethoxybenzaldehydes, vanillin, iso-vanillin, syringaldehyde, ortho-, iso- and

terephthalaldehyde, (2,3)-, (2,4)-, (2,5)-, (2,6)- and
(3,5)-dimethylbenzaldehydes, 4-isopropylbenzaldehyde,
4-dimethylaminobenzaldehyde, 4-diethylaminobenz-
aldehyde, piperonal, (2,6)- and (3,5)-dimethyl-4-
5 hydroxybenzaldehyde, 2,3,4-mononitrobenzaldehydes,
2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-4-methoxy-
benzaldehyde, 2-hydroxy-5-methoxybenzaldehyde,
2-hydroxy-6-methoxybenzaldehyde, 4-methylthiobenz-
aldehyde, (2,3,4)-, (2,4,6)-, (3,4,5)- and (2,4,5)-tri-
10 hydroxybenzaldehydes, methyl 2-, 3- and 4-formyl-
benzoates, 2,3,4-mono(2-hydroxyethoxy)benzaldehydes,
4-nitro-3-hydroxybenzaldehyde, 3-nitro-4-hydroxybenz-
aldehyde, 2-nitro-4-hydroxybenzaldehyde, 3-nitro-
2-hydroxybenzaldehyde, 2,3,4-monotrifluorobenz-
15 aldehydes, 2,3-dihydroxy-4-methoxybenzaldehyde, 3,4-
dihydroxy-5-methoxybenzaldehyde, 3,5-dihydroxy-
4-methoxybenzaldehyde, 3-methoxy-2-nitrobenzaldehyde,
4-methoxy-2-nitrobenzaldehyde, 2-methoxy-3-
nitrobenzaldehyde, 4-methoxy-3-nitrobenzaldehyde,
20 (2,3,4)-, (2,4,6)-, (3,4,5)- and (2,4,5)-
trimethoxybenzaldehydes, 5-nitrovanillin, (2,4)- and
(2,6)-dinitrobenzaldehydes, pentamethylbenzaldehyde,
4-methylsulphonylbenzaldehyde, 2,3,4-monoformyl-
phenoxyacetic acids, 4-diethylaminosalicylaldehyde, 4-
25 (3-dimethylaminopropoxy)benzaldehyde, 2,3-dihydro-
benzo(b)furan-5-carboxaldehyde, 1- and 2-naphth-
aldehyde, 6- and 5-carboxaldehyde-1,4-benzodioxane,
2,4-monohydroxy-1-naphthaldehydes, 1-monohydroxy-2-
naphthaldehyde, 1-(4-formylphenyl)imidazole, 4-
30 pyrrolidinolbenzaldehyde, 2,4-monomethoxy-1-naphth-
aldehydes, 2,3-dimethylchroman-6-carboxaldehyde,
2,3,6,7-tetrahydro-1H,5H-pyrido(3,2,1-IJ)quinoline-9-
carbaldehyde, 4-dimethylamino-1-naphthaldehyde, 9-
anthraldehyde, 3-nitro-4-pyrrolidinobenzaldehyde, 3-
35 nitro-4-piperidinobenzaldehyde, 3-nitro-4-morpholino-
benzaldehyde, pyridine 2,3,4-monocarboxaldehydes, 2,6-
pyridinodicarboxaldehyde, 5-formyl-6-methyluracil,
pyridoxal, quinoline-2,3,4-monocarboxaldehydes,
8-hydroxyquinoline-2-carboxaldehyde, 2- and 3-fur-

aldehydes, 2- and 3-thienylcarboxaldehydes, 2- and 3-imidazocarboxaldehydes, 2-pyrrolicarboxaldehyde, 5-nitro-2-furaldehyde, 5-(dimethylamino)-2-furaldehyde, 2,5 and 2,3-thiophenedicarboxaldehydes, pyrazole-3-carbaldehyde, 5-nitro-2-thiophenecarboxaldehyde, 5-nitro-3-thiophenecarboxaldehyde, indole-3-carboxaldehyde, N-methyl-indole-3-carboxaldehyde, 2-methylindole-3-carboxaldehyde, 4,5,6,7-monomethyl-indolecarboxaldehyde and 5-formyl-2-furansulphonic acid.

The ketones of formulae (XIX) and (XX) can be chosen from 2,3-indolinedione, 2,3-butanedione, 2,3-pentanedione, (2,3)- and (3,4)-hexanedione, 1-phenyl-1,2-propanedione, benzil, furil, 2,2'-pyridil, nitrobenzil, anisil, 3,3'-dimethoxybenzil, 4,4'-bis-(dimethylamino)benzil, camphoroquinone, cyclohexane-1,2-dione, isatin, N-methylisatin, 4-, 5-, 6- and 7-monomethylisatin, (4,5)-, (4,7)-, (5,7)- and (6,7)-dimethylisatin, N-ethylisatin, N-hydroxymethylisatin, 5-, 6- and 7-monomethoxyisatin, 4-, 5-, 6- and 7-monochloroisatin, 4-, 5-, 6- and 7-monobromoisatin, N-isopropylisatin, N-butylisatin, N-propylisatin, 5-nitroisatin, isatin-5-sulphonic acid, 2,4,5-trihydroxypyrimidine, alloxan, 1,3-dimethylhexahydro-2,4,5,6-pyrimidinetetrone, ninhydrin, chinisatin, 1,3-indenedione, squaric acid, croconic acid, 3,4-dimethoxy-3-cyclobutene-1,2-dione, 3- and 4-ethoxy-3-cyclobutene-1,2-dione, 3- and 4-isopropoxy-3-cyclobutene-1,2-dione, 3,4-di-N-butoxy-3-cyclobutene-1,2-dione, rhodizonic acid, oxindole, N-methyl-2-indolinone, N-methylnitro-2-indolinone, 6-methoxyoxindole, 5,6-dimethoxyoxindole and 5- and 6- monochlorooxindole.

The preferred quinones of formulae (XXI) and (XXII) are, inter alia, 1,4-naphthoquinone, spinolusin, atromentin, aurentioglyocladin, 2,5-dihydroxy-6-methylbenzoquinone, 2-hydroxy-3-methyl-6-methoxylbenzoquinone, 2,5-dihydroxy-3,6-diphenylbenzoquinone, 2,3-dimethyl-5-hydroxy-6-methoxybenzoquinone, 2,5-dihydroxy-6-isopropylbenzoquinone, lawsone, juglone,

fafioline, naphthazarine, naphthopurpurine, lapachol, plumbagin, chloroplumbagin, droserone, shikonine, 2-hydroxy-3-methyl-1,4-naphthoquinone, 3,5-dihydroxy-1,4-naphthoquinone, 2,5-dihydroxy-1,4-naphthoquinone, 2-methoxy-5-hydroxy-1,4-naphthoquinone, 3-methoxy-5-hydroxy-1,4-naphthoquinone, (1,4) and (1,2)-naphthoquinone, 4,5-dimethoxy-1,2-benzoquinone, phenanthrenequinone and (1,2)-naphthoquinone-4-sulphonic acid.

The derivatives of formula (XXIII) are represented in particular by 3-imino-3H-isoindolylamine, 3-imino-4-methyl-3H-isoindolylamine, 3-imino-4-tert-butyl-3H-isoindol-1-ylamine, 3-imino-7-nitro-3H-isoindol-1-ylamine, 3-amino-1-imino-1H-isoindol-4-ol, 3-imino-7-isopropoxy-3H-isoindol-1-ylamine, 3-imino-7-(2,2,2-trifluoroethoxy)-3H-isoindol-1-ylamine, 3-imino-7-ethoxy-3H-isoindol-1-ylamine, 3-imino-7-butoxy-3H-isoindol-1-ylamine, 3-amino-1-imino-1H-isoindol-4-sulphonic acid, 3-imino-7-chloro-3H-isoindol-1-ylamine, 3-imino-5-methyl-3H-isoindol-1-ylamine, 3-imino-5-ethyl-3H-isoindol-1-ylamine, 3-imino-5-tert-butyl-3H-isoindol-1-ylamine, 3-imino-5-amino-3H-isoindol-1-ylamine, N-(1-amino-3-imino-3H-isoindol-5-yl)acetamide, 3-imino-5-nitro-3H-isoindol-1-ylamine, 3-imino-5-fluoro-3H-isoindol-1-ylamine, 3-imino-5-chloro-3H-isoindol-1-ylamine, 3-imino-5-methylsulphanyl-3H-isoindol-1-ylamine, 3-imino-5-methoxy-3H-isoindol-1-ylamine, 3-imino-5-ethoxy-3H-isoindol-1-ylamine, 3-imino-5-propoxy-3H-isoindol-1-ylamine, 3-imino-5-isopropoxy-3H-isoindol-1-ylamine, 3-imino-5-butoxy-3H-isoindol-1-ylamine, 3-imino-5-isobutoxy-3H-isoindol-1-ylamine, 3-imino-5-tert-butoxy-3H-isoindol-1-ylamine, 3-imino-5-(2,2,2-trifluoromethyl)-3H-isoindol-1-ylamine, 3-imino-5-(2,2,2-trifluoroethoxy)-3H-isoindol-1-ylamine, 3-imino-5-methanesulphonyl-3H-isoindol-1-ylamine, 3-imino-5,6-dimethyl-3H-isoindol-1-ylamine, 3-imino-5,6-diethyl-3H-isoindol-1-ylamine, 3-imino-5,6-dimethoxy-3H-isoindol-1-ylamine, 3-imino-5,6-diethoxy-3H-isoindol-1-ylamine, 3-imino-5,6-dibutoxy-3H-isoindol-1-ylamine, 3-imino-5,6-

bis(trifluoromethyl)-3H-isoindol-1-ylamine, 3-imino-
5,6-dichloro-3H-isoindol-1-ylamine, 5,6-bis(ethoxy-
methyl)3-imino-3H-isoindol-1-ylamine, 3-amino-1-imino-
1H-isoindole-4,7-diol, 4,7-dichloro-3-imino-3H-iso-
5 indol-1-ylamine, 4,5,7-trichloro-3-imino-N6,N6-di-
methyl-3H-isoindol-1,6-diamine, 4,5,6,7-tetrachloro-
3-imino-3H-isoindol-1-ylamine, 4,5,6,7-tetrafluoro-
3-imino-3H-isoindol-1-ylamine, 3-butylimino-3H-
isoindol-1-ylamine, 2-(3-aminoisoindol-1-ylideneamino)-
10 ethanol, 3-(3-aminoisoindol-1-ylidenamino)-3-methyl-
pentane-1,5-diol, N-(3-aminoisoindol-1-ylidene)-
guanidine, 7-imino-7H-pyrrolo[3,4-b]pyrid-5-ylamine, 7-
imino-7H-pyrrolo[3,4-b]pyrazin-5-ylamine, 7-imino-2,3-
dimethyl-7H-pyrrolo[3,4-b]pyrazin-5-ylamine, 7-imino-
15 7H-[1,4]dithiino[2,3-c]pyrrol-5-ylamine, 7-imino-2,3-
dimethyl-7H-[1,4]dithiino[2,3-c]pyrrol-5-ylamine, 7-
imino-2-methyl-2,3-dihydro-7H-[1,4]dithiino[2,3-
c]pyrrol-5-ylamine, 7-imino-2,3-dihydro-7H-[1,4]dithi-
ino[2,3-c]pyrrol-5-ylamine, 3-aminoisoindol-1-one, 3-
20 amino-7-methylisoindol-1-one, 3-amino-7-hydroxymethyl-
isoindol-1-one, 3-amino-7-chloroisoindol-1-one, 3-
amino-4-chloroisoindol-1-one, 3-amino-1-oxo-1H-iso-
indol-4-sulphonic acid, 3-amino-4-nitroisoindol-1-one,
3-amino-6-nitroisoindol-1-one, 3-amino-6-methyliso-
25 indol-1-one, 3-amino-6-chloro-isoindol-1-one, 3-amino-
6-bromo-isoindol-1-one, 3-amino-6-methylsulphanyl-
isoindol-1-one, 3-amino-6-methoxyisoindol-1-one, 3-
amino-5-chloroisoindol-1-one, 3-amino-5-fluoroisoindol-
1-one, 3-amino-5-methoxyisoindol-1-one, 3-amino-5-
30 nitroisoindol-1-one, ethyl 3-amino-1-oxo-1H-isoindole-
5-carboxylate, 3-amino-5,6-dichloroisoindol-1-one, 3-
amino-5,6-dibromoisoindol-1-one, 3-amino-4,7-dichloro-
isoindol-1-one, 3-amino-4,5,7-trichloroisoindol-1-one,
3-amino-4,5,6,7-tetrachloroisoindol-1-one, 3-amino-
35 4,5,7-trichloro-6-methylsulphanylisoindol-1-one,
3-amino-4,5,6,7-tetrabromoisoindol-1-one, 3-amino-
4,5,6,7-tetrafluoroisoindol-1-one, 3-methylaminoiso-
indol-1-one, 3-ethylaminoisoindol-1-one, 3-propylamino-
isoindol-1-one, 3-dimethylaminoisoindol-1-one, 7-ethyl-

aminopyrrolo[3,4-b]pyrid-5-one, 7-aminopyrrolo[3,4-b]-
pyrid-5-one, 3-aminopyrrolo[3,4-c]pyrid-5-one, 3-amino-
6-methylpyrrolo[3,4-c]pyrid-1-one, 5-aminopyrrolo[3,4-
b]pyrid-7-one, 7-aminopyrrolo[3,4-b]pyrazin-5-one,
5 7-amino-2-methylpyrrolo[3,4-b]pyrazin-5-one, 7-amino-
2,3-dimethylpyrrolo[3,4-b]pyrazin-5-one, 7-amino-2,3-
dihydro[1,4]dithiino[2,3-c]pyrrol-5-one, 3-imino-
2-methyl-2,3-dihydroisoindol-1-one, 3-imino-2-ethyl-
2,3-dihydroisoindol-1-one, 3-imino-2-propyl-2,3-di-
10 hydroisoindol-1-one, 2-hydroxymethyl-3-imino-2,3-di-
hydroisoindol-1-one, 2-(2-hydroxyethyl)-3-imino-2,3-di-
hydroisoindol-1-one, 2-(1-imino-3-oxo-1,3-dihydroiso-
indol-2-yl)ethanesulphonic acid, 3-(1-imino-3-oxo-1,3-
dihydroisoindol-2-yl)propionic acid, 2-(3-hydroxy-
15 propyl)-3-imino-2,3-dihydroisoindol-1-one and 5-imino-
6-methyl-5,6-dihydropyrrolo[3,4-b]pyridin-7-one.

In the context of the present invention:

The halogen atoms preferentially denote a
fluorine, chlorine, bromine or iodine atom.

20 The alkyl, monohydroxyalkyl, polyhydroxyalkyl,
alkylhydroxyalkyl, alkylsulphonyl, carboxyalkyl, amino-
alkyl, alkylaminoalkyl and dihydroxyaminoalkyl radicals
can be linear or branched.

The alkyl groups in particular denote groups of
25 1 to 20 carbon atoms such as, for example, methyl,
ethyl, propyl, isopropyl, n-propyl, butyl, n-butyl,
tert-butyl, pentyl, n-pentyl, isopentyl, n-hexyl, iso-
hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl
and pentadecyl groups. The alkyl groups preferably
30 denote a group of 1 to 6 carbon atoms;
these alkyl groups can be substituted; for example,
with a halogen atom or a cyano or hydroxyl radical, and
can thus represent trifluoromethyl, δ -chloropropyl,
 β -cyanoethyl or β -hydroxyethyl radicals.

35 Among the monohydroxyalkyl groups which may be
mentioned in particular are hydroxymethyl, hydroxy-
ethyl, hydroxypropyl and hydroxybutyl groups.

Among the polyhydroxyalkyl radicals which may
be mentioned in particular are dihydroxyethyl, di-

hydroxypropyl, trihydroxypropyl and dihydroxybutyl radicals.

The alkoxy groups denote a group $-O-R$, R representing an alkyl group as defined above.

5 The alkenyl groups denote a monovalent radical corresponding to the ethylenic carbons, such as, for example, alkyl or 3,3-dimethylallyl.

The acetyloxy groups denote a group $-O-CO-R$, R representing an alkyl group as defined above.

10 Among the cycloalkyl radicals which may be mentioned in particular are cyclohexyl and cyclopentyl.

Among the aryl radicals which may be mono- or polycyclic, mention may be made in particular of phenyl and naphthyl groups.

15 Among the heterocycles, which may be mono- or polycyclic and containing one or more hetero atoms, mention may be made of thiophene, pyrrole, imidazole, pyrazole, triazole, thiazole, furan, benzofuran, benzimidazole, benzothiazole, pyridyl, benzoxazole,
20 quinolyl, quinazolyl, quinoxalyl or naphthyl, rings.

Among the alkylaryl radicals which may be mentioned in particular are benzyl, phenethyl and naphthylmethyl groups.

25 The aminoaryl groups denote groups NHR , R representing an aryl radical.

In the context of the present invention, the cycloalkyl and aryl radicals and the heterocycles may be substituted or polysubstituted, for example with a halogen, with a C_1-C_4 alkyl, a C_1-C_4 alkoxy, a nitro
30 group, a hydroxyl group, a carboxylic group, a C_1-C_4 acetyloxy group, a carboxamide group, a sulphonamide, sulphonic, nitrile, $-CF_3$ or $-OCF_3$ group or with a cycloalkyl or aryl radical which may be substituted with a C_1-C_4 alkyl.

35 In the context of the present invention, the formulae (I) to (XXIII) are not limited to those specifically described, but also comprise the tautomeric forms thereof, when they exist.

For the purposes of the present invention, the cosmetically acceptable salts of the abovementioned compounds can be hydrochlorides, sulphates, hydrobromides or tartrates.

5 The compositions for dyeing keratin fibres, in particular human keratin fibres such as the hair, in accordance with the present invention are essentially characterized in that they comprise at least one compound containing active methylene as defined above
10 and at least one compound chosen from an aldehyde of formula (XVIII), a ketone of formula (XIX) or (XX), a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative as defined above, in a medium which is suitable for dyeing.

15 The compound containing active methylene in these compositions is preferably chosen from benzofuran(2H)one, benzoylacetonitrile, 5-amino-2H-pyrazol-3-ol and 4-imino-4,5-dihydrothiazol-2-ylamine.

 In one preferred embodiment of the invention,
20 the compound chosen from an aldehyde of formula (XVIII), a ketone of formula (XIX) or (XX), a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative is chosen from naphthoquinone, isatin, N-methylisatin, 3-imino-3H-isoindol-1-ylamine, 4-
25 dimethylaminobenzaldehyde and 4-dimethylaminonaphthaldehyde.

 The compound containing active methylene may be present in a concentration ranging from 0.01% to 10%, and preferably from 0.05% to 5%, by weight relative to
30 the total weight of the composition.

 The compound chosen from an aldehyde of formula (XVIII), a ketone of formula (XIX) or (XX), a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative can be present in a concentration ranging
35 from 0.01% to 10%, and preferably from 0.05% to 5%, by weight relative to the total weight of the composition.

 The medium which is suitable for dyeing is preferably an aqueous medium consisting of water and/or of cosmetically acceptable organic solvents, and more

particularly alcohols such as ethyl alcohol, isopropyl alcohol, benzyl alcohol and phenethyl alcohol, or glycols or glycol ethers such as, for example, ethylene glycol and its monomethyl, monoethyl and monobutyl
5 ethers, propylene glycol or its ethers such as, for example, propylene glycol monomethyl ether, butylene glycol, dipropylene glycol and diethylene glycol alkyl ethers such as, for example, diethylene glycol monoethyl ether or monobutyl ether, in concentrations
10 of between about 0.5% and 20%, and preferably between about 2% and 10%, by weight relative to the total weight of the composition.

Fatty amides such as mono- and diethanolamides of acids derived from copra, of lauric acid or of oleic
15 acid can also be added to the composition according to the invention, in concentrations of between about 0.05% and 10% by weight.

Surfactants that are well known in the prior art and of anionic, cationic, nonionic, amphoteric or
20 zwitterionic type or mixtures thereof can also be added to the composition according to the invention, preferably in a proportion of between about 0.1% and 50% by weight and advantageously between about 1% and 20% by weight relative to the total weight of the
25 composition.

Thickeners can also be used in a proportion ranging from about 0.2% to 20%.

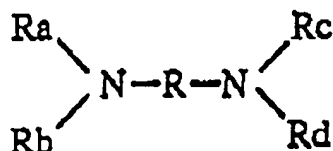
The said dye composition can also contain various common adjuvants such as antioxidants, frag-
30 rances, sequestering agents, dispersants, hair conditioners, preserving agents and opacifiers, as well as any other additive usually used in the dyeing of keratin substances.

Needless to say, a person skilled in the art
35 will take care to select the optional additional compound(s) mentioned above, such that the advantageous properties intrinsically associated with the dye composition according to the invention are not, or are

not substantially, adversely affected by the addition(s) envisaged.

The dye composition according to the invention can be formulated at acidic, neutral or alkaline pH, it being possible for the pH to vary, for example, from 2 to 11 and preferably from 5 to 10, and it being possible for it to be adjusted by means of basifying or acidifying agents or buffers that are previously well known.

Basifying agents which may be mentioned are aqueous ammonia, alkaline carbonates, alkanolamines, for example mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula:



in which R is a propylene residue optionally substituted with a hydroxyl group or a C₁-C₄ alkyl radical; Ra, Rb, Rc and Rd, simultaneously or independently of each other, represent a hydrogen atom or a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical.

The acidifying agents are conventionally mineral or organic acids such as, for example, hydrochloric acid, tartaric acid, citric acid and phosphoric acid.

Among the buffers which may be mentioned, for example, is potassium dihydrogen phosphate / sodium hydroxide.

The composition applied to the hair can be in various forms, such as in the form of a liquid, cream or gel or in any other form which is suitable for dyeing keratin fibres. In particular, it can be packaged under pressure in an aerosol can in the presence of a propellant and can form mousse.

In accordance with the present invention, the process for dyeing keratin fibres, in particular human keratin fibres such as the hair, is essentially

characterized in that a component (A) consisting of a composition containing, in a medium which is suitable for dyeing, at least one compound containing active methylene as defined above, and a component (B) consisting of a composition containing, in a medium which is suitable for dyeing, at least one compound chosen from an aldehyde of formula (XVIII), a ketone of formula (XIX) or (XX), a quinone and a diiminoisoindoline or 3-aminoisoindolone derivative such as, for example, one of those defined above, is applied to the said fibres so as to allow the development of a coloration on the said keratin fibres.

In one preferred embodiment of the process of the invention, the components (A) and (B) are mixed together just before use, and the resulting composition is then applied immediately to the keratin fibres, and is left to act on them for 1 to 60 minutes and preferably from 1 to 30 minutes; the keratin fibres are then rinsed, washed with shampoo, rinsed again and then dried.

Another process of the present invention consists essentially in applying component (A) to the keratin fibres, followed or preceded by application of component (B) to the said fibres, in leaving each component to act for 1 to 60 minutes and preferably from 1 to 30 minutes, and in optionally rinsing with water between each application; the keratin fibres are then rinsed, washed with shampoo, rinsed again and then dried.

A subject of the invention is also an agent for dyeing keratin fibres, in particular human hair, characterized in that it consists of components (A) and (B) stored separately, as defined above.

Components (A) and (B) are intended either to be mixed together immediately before use or to be applied successively to the fibres to be treated.

According to one embodiment, the various components (A) and (B) can be packaged in a multi-compartment device also known as a "dyeing kit"

comprising all the components intended to be applied for the same dyeing operation on keratin fibres, in particular human keratin fibres such as the hair, in successive applications with or without premixing.

5 Such devices can comprise a first compartment containing component (A) containing the compound containing active methylene and a second compartment containing component (B) containing the compound chosen from an aldehyde, a ketone, a quinone and a
10 diiminoisoindoline or 3-aminoisoindolone derivative.

 Another variant can also consist in storing component (A) or component (B) in an anhydrous solvent medium and in providing a third compartment containing
15 a cosmetically acceptable aqueous medium which is suitable for dyeing. In this case, the contents of the third compartment are mixed, immediately before use, into one or other of the two compartments containing the anhydrous components (A) and (B), or alternatively the three compartments are mixed together before use.

20 Concrete examples illustrating the invention will now be given.

EXAMPLES

Example 1

The dye composition below was prepared just
5 before use:

3-imino-3H-isoindol-1-ylamine	0.435 g
benzofuran-(2H)-one	0.402 g
ethyl alcohol	30.0 g
water	qs 100 g

10

The above composition was applied to locks of natural grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a lemon
15 yellow shade.

Example 2

The dye composition below was prepared just
before use:

20 4-dimethylaminobenzaldehyde	0.447 g
benzofuran-(2H)-one	0.402 g
ethyl alcohol	30.0 g
water	qs 100 g

25

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a bright orange shade.

30

Example 3

The dye composition below was prepared just
before use:

1,4-naphthoquinone	0.447 g
35 benzofuran-(2H)-one	0.402 g
ethyl alcohol	30.0 g
water	qs 100 g

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a dark violet shade.

Example 4

The dye composition below was prepared just before use:

10	isatin	0.441 g
	benzofuran-(2H)-one	0.402 g
	ethyl alcohol	30.0 g
	water	qs 100 g

15 The above composition was applied to locks of bleached hair, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a coppery shade.

20 **Example 5**

The dye composition below was prepared just before use:

	3-imino-3H-isoindol-1-ylamine	0.435 g
	benzoylacetonitrile	0.435 g
25	ethyl alcohol	30.0 g
	water	qs 100 g

30 The above composition was applied to locks of bleached hair, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a mustard-yellow shade.

Example 6

35 The dye composition below was prepared just before use:

	4-dimethylaminobenzaldehyde	0.447 g
	benzoylacetonitrile	0.402 g
	ethyl alcohol	30.0 g
	water	qs 100 g

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After
5 rinsing with running water and drying, the hair was a bright red-orange shade.

Example 7

The dye composition below was prepared just
10 before use:

1,4-naphthoquinone	0.474 g
benzoylacetonitrile	0.435 g
ethyl alcohol	30.0 g
water	qs 100 g

15

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After
20 rinsing with running water and drying, the hair was a hazelnut shade.

Example 8

The dye composition below was prepared just before use:

25 isatin	0.441 g
benzoylacetonitrile	0.435 g
ethyl alcohol	30.0 g
water	qs 100 g

30

The above composition was applied to locks of bleached hair, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a red-coppery shade.

35 **Example 9**

The dye composition below was prepared just before use:

3-imino-3H-isoindol-1-ylamine	0.435 g
6-hydroxybenzofuran-(2H)-one	0.450 g

ethyl alcohol		30.0	g
water	qs	100	g

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a golden yellow shade.

10 **Example 10**

The dye composition below was prepared just before use:

4-dimethylaminobenzaldehyde		0.447	g
6-hydroxybenzofuran-(2H)-one		0.450	g
15 ethyl alcohol		30.0	g
water	qs	100	g

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was an orange-yellow shade.

Example 11

25 The dye composition below was prepared just before use:

1,4-naphthoquinone		0.474	g
6-hydroxybenzofuran-(2H)-one		0.450	g
ethyl alcohol		30.0	g
30 water	qs	100	g

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a hazelnut shade.

Example 12

The dye composition below was prepared just before use:

	isatin	0.441 g
5	6-hydroxybenzofuran-(2H)-one	0.450 g
	ethyl alcohol	30.0 g
	water	qs 100 g

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a coppery slightly yellow shade.

Example 13

The dye composition below was prepared just before use:

	3-imino-3H-isoindol-1-ylamine	0.435 g
	5-amino-2H-pyrazol-3-ol	0.297 g
20	ethyl alcohol	30.0 g
	water	qs 100 g

The above composition was applied to locks of bleached hair, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a golden-beige shade.

Example 14

The dye composition below was prepared just before use:

30	4-dimethylaminobenzaldehyde	0.447 g
	5-amino-2H-pyrazol-3-ol	0.297 g
	ethyl alcohol	30.0 g
	water	qs 100 g

35

The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After

rinsing with running water and drying, the hair was a orange-yellow shade.

Example 15

5 The dye composition below was prepared just before use:

1,4-naphthoquinone	0.474 g
5-amino-2H-pyrazol-3-ol	0.297 g
ethyl alcohol	30.0 g
10 water	qs 100 g

15 The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a golden brown shade.

Example 16

20 The dye composition below was prepared just before use:

3-imino-3H-isoindol-1-ylamine	0.435 g
3-amino-1-phenyl-2-pyrazolin-5-one	0.525 g
ethyl alcohol	30.0 g
25 water	qs 100 g

30 The above composition was applied to locks of natural grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a green-yellow shade.

Example 17

35 The dye composition below was prepared just before use:

4-dimethylaminobenzaldehyde	0.447 g
3-amino-1-phenyl-2-pyrazolin-5-one	0.525 g
ethyl alcohol	30.0 g
water	qs 100 g

The above composition was applied to locks of bleached hair, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a bright orange shade.

5

Example 18

The dye composition below was prepared just before use:

	1,4-naphthoquinone	0.474 g
10	3-amino-1-phenyl-2-pyrazolin-5-one	0.525 g
	ethyl alcohol	30.0 g
	water	qs 100 g

15 The above composition was applied to locks of permanent-waved grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a dark brown shade.

20 **Example 19**

The dye composition below was prepared just before use:

	3-imino-3H-isoindol-1-ylamine, HCl	0.435 g
	4-imino-4,5-dihydrothiazol-2-ylamine	0.454 g
25	ethyl alcohol	30.0 g
	water	qs 100 g

30 The above composition was applied to locks of natural grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a bright orange shade.

Example 20

35 The dye composition below was prepared just before use:

	3-imino-3H-isoindol-1-one	0.438 g
	4-imino-4,5-dihydrothiazol-2-ylamine HCl	0.454 g
	ethyl alcohol	30.0 g

water	qs	100	g
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The above composition was applied to locks of natural grey hair containing 90% white hairs, and was left to stand on the hair for 30 minutes. After rinsing with running water and drying, the hair was a yellow shade.

Example 21

10 The dye composition below was prepared just before use:

4-dimethylaminobenzaldehyde	0.447	g
4-imino-4,5-dihydrothiazol-2-ylamine HCl	0.454	g
ethyl alcohol	30.0	g
15 water	qs	100 g
[lacuna]		